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NANO-REINFORCED CONCRETE: AN INTELLIGENT AND HIGH PERFORMANCE CONSTRUCTION MATERIAL

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ABSTRACT

Like other important scientific and engineering disciplines, nanotechnology is also being applied widely to civil engineering, especially in construction applications. Concrete, which is the most frequently used construction material, suffers from its inherent brittleness and vulnerability towards degradation and therefore, attempts have been made to improve its performance through reinforcement of nanomaterials. Additionally, nanomaterials incorporation within concrete makes it intelligent by introducing properties like piezoresistivity and self-sensing, self-cleaning, etc. In this context, the present paper presents a brief overview of the latest developments in the nano-reinforced (mainly carbon nanofibre and nanotube reinforced) concrete materials.

Keywords: Carbon nanomaterials, concrete, dispersion, microstructure, mechanical properties, durability

INTRODUCTION

Cementitious materials are characterized by quasi-brittle behaviour and susceptible to cracking. The cracking process within concrete begins with isolated nano-cracks, which then conjoin to form micro-cracks and in turn macro-cracks. Formation of cracks reduces the mechanical properties of concrete and makes it prone towards various degradation conditions such as chemical attack, high moisture, sea water, etc. This leads to reduced durability of concrete structures. Reinforcement is required because of this brittle nature of concrete and as reinforcements, polymeric fibers as well as glass and carbon fibers were used during 1970's, 80's and 90's respectively. Recently the use of microfiber reinforcements has led to significant improvement in the mechanical properties of cement based materials by delaying the transformation of micro-cracks into macro form but could not stop their growth. This fact encouraged the use of nanosize fibers or particles for concrete reinforcement in order to prevent the growth of nano-cracks transforming in to micro-cracks. Nanoparticle addition in cement paste was found to improve mechanical, chemical and thermal properties of cementitious matrix. There are various types of nanoparticles, especially SiO_2 and Fe_2O_3, which when incorporated in to cement led to considerable improvement in the compressive strength. Nano-sized TiO_2 has been added to accelerate the rate of hydration and increase the degree of hydration (Lee, 2010). Moreover, the photo-catalytic characteristic of TiO_2 helped to remove the organic pollutants from concrete surfaces, which are directly exposed to UV radiation (Cassar, 2005). Extensive research endeavors over the last few years demonstrated the application potential of various carbon nanomaterials, mainly carbon nanofibre (CNF) and carbon nanotube (CNT), in concrete in order to utilize their extraordinary mechanical, electrical and thermal properties. In nano-scale, CNFs and CNTs offer the possibility to restrict the formation as well as growth of nano-cracks within concrete, thus creating a new generation of crack free materials (Sanchez, 2009). Moreover, reinforcement of cementitious materials with CNF and CNT introduces electrical conductivity as well as piezoresistivity and as a result, nano-reinforced concrete became an intelligent material being able to sense its own deformation and damage, so that preventive measures can be taken to avoid further degradation and sudden collapse (Yu, 2009).

DISPERSION OF CNF/CNT IN CEMENTITIOUS MATRIX

Similar to polymeric matrices, dispersion of carbon nanomaterials in cementitious matrices is also a critical issue which strongly influences the properties of cement based nanocomposites. The approach of dispersing CNF/CNT directly within cement paste during mixing is not feasible, as the thickening of cement paste begins within a short period after addition of water (Gopalakrishnan, 2011). The mixing process using a Hobart mixer, commonly used to prepare mortar paste cannot ensure proper dispersion of CNT within cementitious matrix. In a recent research performed by Cota et al. (Cota, 2012), presence of large CNT clusters was visible in a hydrated cement paste, when CNTs were mixed with cement using a Hobart mixer. Presence of these CNT clusters resulted in increase in porosity and decrease in mechanical properties. To avoid this situation, the strategy commonly employed for mixing CNTs/CNFs with cementitious matrices is to disperse these nanomaterials first in water, followed by mixing of nanomaterial/water dispersion with cement using a conventional mixer. The methods of dispersing nanomaterials in water should be carefully selected so that they do not interfere with the processing of cement nanocomposites. Many surfactants that are successfully used to disperse carbon nanomaterials in polymeric matrices have been reported to create problems in cement hydration, entrap air in the cement paste or react with the water reducing admixtures (Yazdanbakhsh, 2009).

Dispersion of CNF/CNT in cement is even more difficult as compared to the polymeric matrices. One of the reasons for poor dispersion may be the size of cement grains. As CNFs or CNTs are separated by the cement grains, the presence of larger grains than the average leads to non uniform distribution of nanomaterials throughout the matrix (Yazdanbakhsh, 2010). Fig. 1 shows the SEM micrograph of Portland cement particles. It can be seen that there exists a significant difference in the size of various particles and some particles are present with size more than 100 μ. Presence of these large cement grains leads to absence of CNFs/CNTs in some areas, whereas they can be present in higher quantity in other areas where the cement grains are much smaller in size. This results in non-homogeneous dispersion of nanomaterials throughout the matrix. Although reduction of cement particle size using ball milling can improve nanomaterial dispersion, small grain cement has many other disadvantages such as high water consumption, thermal cracking, more chemical and autogenous shrinkage, etc. (Bentz, 1999; Mehta, 1997). Therefore, to improve carbon nanomaterial dispersion in cementitious matrices various approaches have been tried till date, considering the issues discussed above. These dispersion techniques can be broadly categorized as physical and chemical techniques and are discussed in detail in the following sections.

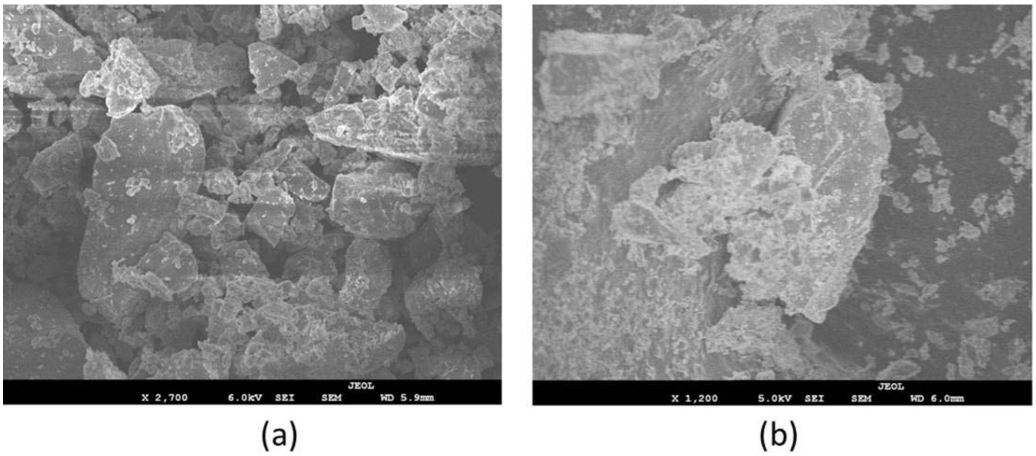

Fig. 1. SEM micrograph of type I Portland cement particles with average size of 10 μ (a) and a particle with size more than 100 μ (b)

PHYSICAL DISPERSION ROUTES

ULTRASONICATION

Ultrasonication is the most frequently used technique to disperse nanomaterials in various polymeric matrices. This technique have been used either alone, or have been combined with other techniques to reduce treatment time and associated problems such as rupture of nanomaterials. In an ultrasonic processor, electrical voltage is converted to mechanical vibrations, which are transferred to the liquid medium (water or solvent) and leads to formation and collapse of microscopic bubbles. During this process (known as cavitation) millions of shock waves are created and a high level of energy is released (Gopalakrishnan, 2011), leading to dispersion of nanomaterials in the liquid. Recently, Yazdanbakhsh et al. (Yazdanbakhsh, 2010) used ultrasonication technique to prepare CNF based cementitious composites. Vapour grown CNFs (1.14 wt.%) were first dispersed in water mixed with a polycarboxylate based superplasticizer (1.71%), using a titanium probe (1/2 inch diameter) ultrasonicator, operated at 20 kHz frequency and amplitude setting of 50%. It was observed that CNFs were dispersed homogeneously after 15 minutes of ultrasonic treatment as shown in Fig. 2 (b). On the contrary, the dispersion prepared through only hand-shaking contained dense CNF clusters and was not homogeneous. However, the fracture surface of cement nanocomposites revealed that the distribution of CNFs in the nanocomposites was not homogeneous. There existed many areas without CNFs as well as areas where CNFs were agglomerated. Therefore, a homogeneous CNF dispersion in water could not guarantee a uniform dispersion in nanocomposites as well. This was probably attributed to the low stability of dispersed CNFs, leading to re-agglomeration during nanocomposite preparation. Hence, ultrasonication has been frequently combined with other chemical methods to ensure homogeneous dispersion as well as to improve dispersion stability.

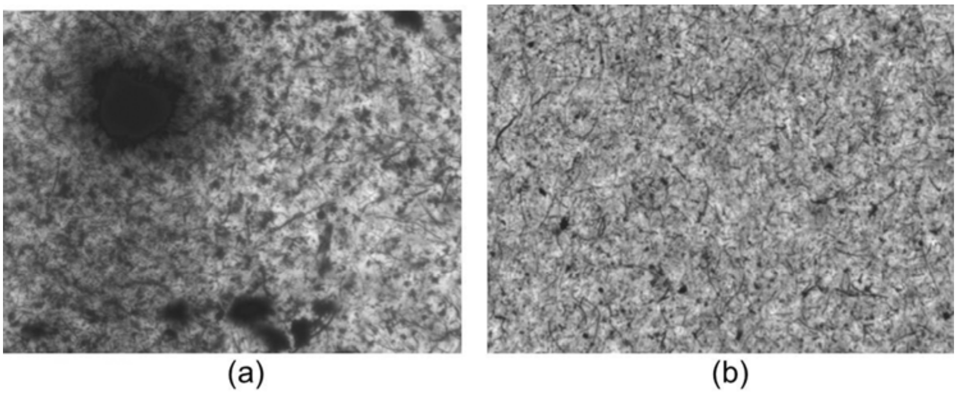

Fig. 2. CNF dispersion in aqueous medium prepared using (a) hand-shaking and (b) sonication for 15 min

ULTRACENTRIFUGE TECHNIQUE

Metaxa et al. (Metaxa, 2012) have recently developed a technique for producing highly concentrated MWCNT /water suspensions that can be used for developing cement nanocomposites at large scale. In this process, MWCNTs were homogeneously dispersed in water using surfactant (MWCNT to surfactant weight ratio of 4.0) using a tip sonicator. When this CNT dispersion was centrifuged at 28,000 rpm using a swing bucket rotor holding centrifuge tubes of 38 ml capacity, the dispersed MWCNTs started precipitating at the bottom of the tube and complete sedimentation was achieved after 11 hours. The supernatant solution was then decanted down to keep only 20% of the initial volume of the solution and CNTs were re-dispersed in this solution through ultrasonication for 40 mins. Optical absorbance spectroscopy revealed that the concentration of MWCNTs increased 5 times using this process. The concentrated MWCNT solution, when diluted by adding the same amount of water previously decanted, showed same concentration as the reference non-concentrated MWCNT suspension. Moreover, it was quite interesting to note that, the cementitious nanocomposites prepared using the concentrated MWCNT suspension (after dilution) exhibited similar mechanical properties as that obtained using the reference non-concentrated MWCNT suspensions, indicating that the dispersion of MWCNTs was preserved even after the concentration process through centrifugation. Therefore, this process can be utilized to prepare large scale production of CNT admixtures for developing cementitious nanocomposites.

CHEMICAL DISPERSION ROUTES

USING SURFACTANT

Surfactants have been widely used to disperse CNTs/CNFs in various polymeric matrices. A surfactant is an amphiphilic compound containing a hydrophilic head and a hydrophobic tail. When used in an aqueous dispersion, the hydrophobic parts of surfactant molecules are adsorbed on the surface of nanomaterials, whereas the hydrophilic parts reduce the surface tension and lead to dispersion of nanomaterials in water. Moreover, due to the presence of surfactant molecules on the surface, the nanomaterial dispersion becomes stable as a result of electrostatic and/or steric repulsion between the surfactant molecules. The influence of surfactant and its concentration on the dispersion of MWCNTs in cement nanocomposites have been investigated by Konsta-Gdoutos et al. (Konsta-Gdoutos, 2010). MWCNT suspensions in water were prepared using a 500W cup-horn high intensity ultrasonic processor operated at an amplitude of 50%, energy of 1900-2100 J/min and at cycles of 20s. 0.16 wt. % of long MWCNTs was dispersed in water using different concentrations of the surfactant (surfactant to MWCNT weight ratios of 1.5, 4.0, 5.0 and 6.25). It was observed that the viscosities of plain cement paste and cement paste containing MWCNTs, dispersed using sonication were similar, whereas the viscosity of cement paste in which MWCNTs were dispersed without sonication was significantly higher at low shear stresses. This was attributed to the presence of agglomerated CNTs in the dispersions prepared without sonication. However, at higher shear stresses, probably the MWCNT agglomerates broke down due to fluid motions and the viscosity in all cases became similar.

It was also observed that at lower surfactant concentrations (surfactant to MWCNT weight ratio 0 and 1.5), large CNT clusters were present in the fracture surface, indicating poor dispersion, as shown in Fig. 3(a) and (b). On the contrary, when higher concentrations of surfactant were used (surfactant to MWCNT weight ratio 4.0 and 6.25), only individual CNTs were identified in the fracture surface, indicating homogeneous dispersion [Fig. 3 (c) and (d)]. Similarly, vapour-grown CNFs (0.048 wt. of cement), when dispersed using the above process with a surfactant to CNF ratio of 4.0, showed very good dispersion in cement (Metaxa, 2010).

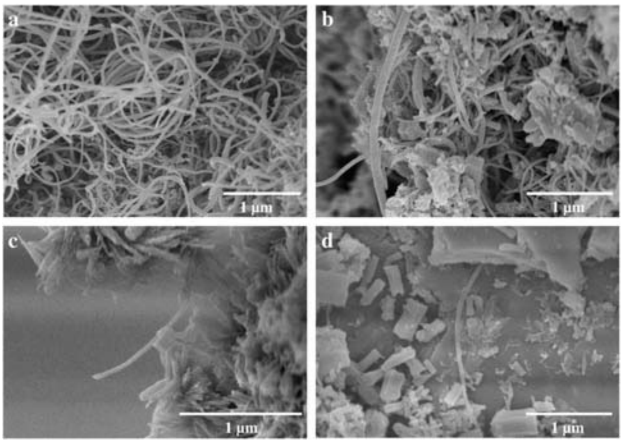

Fig. 3. Dispersion of MWCNT within cementitious composites prepared using different surfactant to MWCNT weight ratio: (a) 0, (b) 1.5, (c) 4.0 and (d) 6.25

It has been reported that the dispersion ability of surfactant also depends on the type of surfactant. It a study conducted by Luo et al. (Luo, 2009), MWCNTs were dispersed in water using five different types of surfactant namely sodium dodecyl benzene sulfonate (SDBS), sodium deoxycholate (NaDC), Triton X-100 (TX10), Arabic gum (AG), and cetyltrimethyl ammonium bromide (CTAB) at a concentration of 2 wt. % (of water). The dispersion was prepared through magnetic stirring for 10 min at 300 rpm, followed by ultrasonication with a tip sonicator (40W) for 90 rounds, each of 90s and 10s rest between the rounds. It was observed that among the various surfactants, SDBS (anionic) provided the best dispersion, which was stable after 70 minutes of ultracentrifugation and 60 days of sitting. The result was even better when SDBS was used in combination with TX10 (non-ionic) in the weight ratio of 3:1. The better stabilization in case of SDBS was attributed to the benzene ring in the hydrophobic chain, smaller chargedSO_3^{2-} head group, and relatively longer alkyl hydrophobic chain (Islam, 2003). The dispersion ability of various surfactants was found in the following order: SDBS&TX10 >SDBS >NaDC &TX10 >NaDC >AG >TX10>CTAB. The cationic surfactant CTAB showed the lowest dispersion capability because of the absence of benzene ring on the long chain and the positive charge which might have neutralized the negative charge of MWCNTs in aqueous solution. The fracture surface of cement nanocomposite containing 0.2 wt.% MWCNTs dispersed using SDBS/TX10 combination showed very uniform distribution of CNTs.

Yu et al. (Yu, 2009) carried out dispersion of MWCNTs (0.1 wt. %) in sodium dodecyl sulfate (SDS) solution (0.2 wt. %) using ultrasonication and subsequently, mixed with water to prepare cement nanocomposites. It was observed that CNTs dispersed using this route was well connected to provide electrical conductivity and piezoresistivity. However, as compared to the acid treated CNTs dispersed without surfactant, the piezoresistive behaviour was inferior, due to the blocking of electrical connections between CNTs by surfactant molecules.

USING POLYMERS AND ADMIXTURES

Various polymers have been used to decorate the surface of carbon nanomaterials through wrapping, so that the nanomaterials will be dispersed easily in various matrices, due to the steric repulsion induced by the polymers. Cwirzen et al. (Cwirzen, 2008) prepared MWCNT/cement nanocomposites through dispersion of MWCNTs in water using ultrasonication and polyacrylic acid polymer and subsequent mixing of the prepared dispersion with cement paste. MWCNTs (0.023-0.14 wt.%) were dispersed in water using ultrasonication for two minutes at 50 Hz, followed by addition of polymer (2.1 wt.% of water) and sonication for another 30 seconds. The surface of MWCNTs became covered with the polymer as shown in Fig. 4 and, the presence of polymer led to a very good dispersion of CNTs in water.

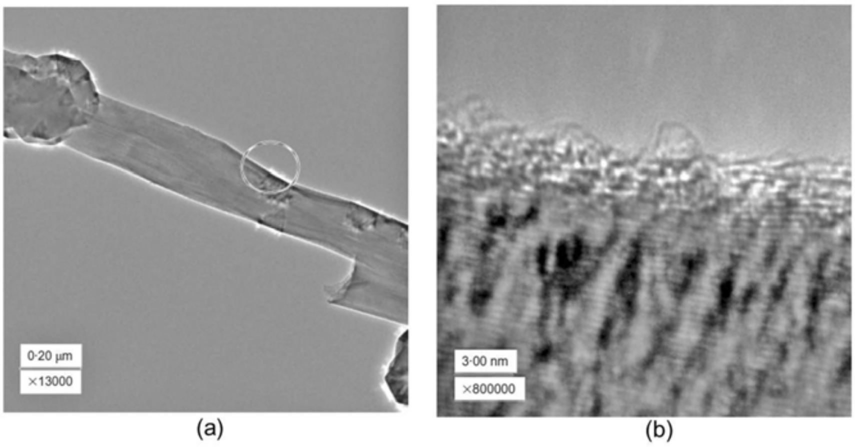

Fig. 4. TEM image of MWCNTs showing presence of acrylic acid polymer on the surface at magnifications of 130000 x (a) and 800000 x (b)

Use of polycarboxylate was also found effective in dispersing CNT in cement by Colloins et al. (Collins, 2012). They have studied the dispersion ability of seven different types of cement admixture such as alkylbenzene sulfonic acid (air entraining agent), styrene butadiene rubber co-polymer latex, aliphatic propylene glycol ether including ethoxylated alkylphenol, polycarboxylate, calcium naphthalene sulfonate, naphthalene sulphonic acid derivatives and lignosulfonate. The dispersions were prepared through magnetic stirring of 0.05 gm CNT in 50 ml water using 0.5-1.5 ml chemical admixture, followed by ultrasonication in a bath sonicator (150 W) for 12 mins. From the sedimentation test it was observed that the use of air entrainer, polycarboxylate and lignosulfonate provided good aqueous dispersions of MWCNT, which were stable up to 9 days. However, the doses of lignosulfonate necessary for good CNT dispersion was reported to delay the setting time of Portland cement (Rixom, 1999). Also, despite of a good aqueous dispersion, the use of alkylbenzene sulfonic acid based air entrainer could not lead to a homogeneous CNT dispersion the in hardened cement paste. This was probably attributed to the lower stability of CNT dispersion and resulting agglomeration during composite processing. On the contrary, the use of polycarboxylate resulted in a very good dispersion of MWCNT in water as well as in the hardened cement paste and therefore, proved to be the best dispersant among the various admixtures used in cement.

Use of methylcellulose for dispersing CNTs in water for preparing cementitious composites has been reported by Veedu et al. (Veedu, 2010). Methylcellulose was first dispersed in water at 80-90°C and then cooled down. CNTs were dispersed in a solvent such as ethanol using ultrasonication and then added to the methylcellulose solution and mechanically stirred. The CNT dispersion using this process was stable for several months. Methylcellulose has also been used by Azhari et al. (Azhari, 2008) to disperse CNTs and prepare piezoresistive cement nanocomposites.

Silica fume is an amorphous polymorph of silicon dioxide and this admixture is used as pozzolanic material in concrete production (Chung, 2002). Silica fume consists of spherical particles with average diameter of 150 nm. Previously silica fume has been found to improve the dispersion of microfibers within cement (Chung, 2005). Sanchez et al. (Sanchez, 2009) studied the influence of silica fume on the dispersion of CNFs in Portland cement. To prepare the cementitious composites, CNFs (up to 2 wt. %) were dry mixed with cement using a conventional three speed mortar mixer. Silica fume (10 wt.%) was next added and dry mixed for 3 min, followed by slow addition of water and mixing for another 6 min. It was observed that silica fume was dispersed within the composites as agglomerates and CNFs were dispersed as agglomerates or pockets as well as individual nanofibres. Previous research of the same authors (Sanchez, 2009) showed that only CNF pockets were observed on fracture surface of cementitious composites in absence of silica fume. The better dispersion in the presence of silica fume was attributed to the smaller size (100 times smaller as compared to anhydrous cement particles) of silica fume particles which could disrupt the van der Waals forces between individual CNFs, thereby mechanically separating some of them during the dry mixing process and reducing the CNF clumps. Additionally, the silica fume particles present within the CNF clumps as well as individual CNFs could also act as the silicon source for the formation of Ca-Si rich phases and nucleation sites for the self-assembly of Ca-Si rich phases.

THROUGH COVALENT FUNCTIONALIZATION

The most common approach to improve the dispersion ability of CNTs/CNFs in water or polymeric matrices is the covalent functionalization. Frequently, carbon nanomaterials have been treated with strong acids such as nitric acid or mixture of sulphuric and nitric acid (3:1) to oxidize the surface and create functional groups such as carboxylic. The negative charge on the carboxylic groups induces electrostatic repulsion between the functionalized nanomaterials and helps in their dispersion as well as to improve dispersion stability. However, the covalent functionalization route often creates defects in the structure of nanomaterials and reduces their aspect ratio, deteriorating their inherent properties.

Therefore, the conditions of the covalent functionalization process needs to be optimized to ensure minimum damage to the nanomaterials.

In a study carried out by Li et al. (Li, 2007), MWCNTs were surface treated using 3:1 mixture of sulphuric acid and nitric acid in a ultrasonic bath for 3 hours and, 0.5 wt.% of surface functionalized CNTs were used to fabricate cementitious composites. It was observed that functionalized CNTs were individually dispersed in cement and tightly wrapped by C-S-H phase of cement matrix, due to covalent bonding between COOH or C-OH groups of nanotubes and C-S-H, as also confirmed by FTIR analysis. Similar observations were also made by Sanchez et al. (Sanchez, 2009) in case of functionalized CNFs using 70% nitric acid. Surface treated CNFs were observed individually dispersed and anchored to the C-S-H phase in 0.5 wt. % CNF/cement nanocomposites. Li et al. (Li, 2005) observed that both untreated and surface treated CNTs, obtained through oxidation using a mixture of H_2SO_4 and HNO_3, could be dispersed well using a rotary mixer and ultrasonication. However, noticeable difference between the morphology of untreated and treated CNT dispersion was observed. Untreated CNTs were well connected to form a three dimensional network, whereas the treated CNTs could not form a three dimensional network due to much fewer contact points and their surface was covered by C-S-H. This difference in dispersion morphology of treated and untreated CNTs was found to have significant effect on the electrical and piezoresistive properties of cement nanocomposites. Surface functionalized MWCNTs were also used by Yu et al. (Yu, 2009) to fabricate piezoresistive cement nanocomposites.

Nasibullina et al. (Nasibullina, 2012) carried out functionalization of few-walled CNTs (FWCNTs) using HNO_3/H_2SO_4mixture and subsequently, washed with acetone to remove formed carboxylated carbonaceous fragments (CCFs), which are organic molecules consisting condensed aromatic rings with several functional groups. Although CCFs have functional groups which can react with cement but, they do not contribute to the mechanical properties due to absence of their structural component. 0.12 wt.% CNT, both containing CCFs and free from CCFs showed uniform dispersion in water, whereas both the dispersion resulted in floccules formation when $Ca(OH)_2$ was added to the dispersion, indicating reaction between the surface functional groups of CNT and Ca^{2+} ions. The hydration of cement on the surface of functionalized CCF free CNTs was also demonstrated by the authors using TEM, as shown in Fig. 5. The TEM image showed the precipitation of C-S-H hydration products on the surface of CNTs, as they acted as the nucleation sites.

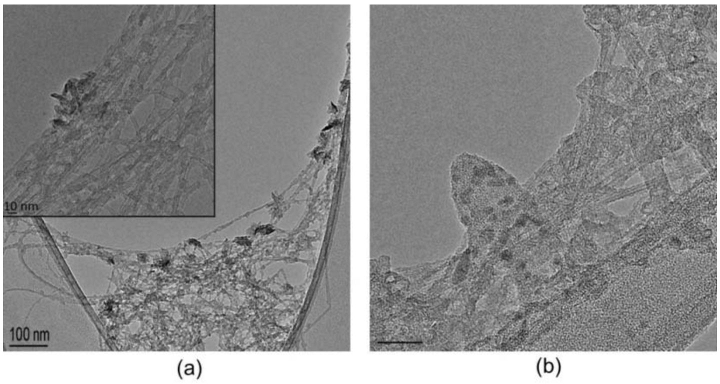

Fig. 5. TEM image of CCF free FWCNTs after hydration for 1 hour (a) and 5.5 hour (b)

USING COMBINATION OF SURFACE FUNCTIONALIZATION AND POLYMERS

To improve the dispersion of carbon nanomaterials within cementitious composites, surface functionalization has also been used in combination with polymers. According to Cwirzen et al (Cwirzen, 2008), the dispersion of functionalized MWCNTs prepared using acrylic acid polymer has much better stability as compared to that obtained using only functioned CNTs or polymers. The dispersion of non-functionalized MWCNTs using acrylic acid polymer or gum arabic was stable only up to 2 hours after which sedimentation was observed. Similarly, aqueous dispersion of functionalized nanotubes also showed poor long term stability. On the contrary, functionalized MWCNTs dispersion prepared using acrylic acid polymer showed stability more than 2 months. The long polyacrylic acid polymers were adsorbed on the surface of functionalized nanotubes and increased the steric barrier towards their agglomeration.

USING COMBINATION OF FUNCTIONALIZATION AND SURFACTANT

An effective dispersion of carboxyl functionalized MWCNTs (up to 0.5 wt.%) in cement was achieved by Han et al. (Han, 2012) through the use of sodium dodecylbenzene sulfonate (NaDDBS) surfactant. MWCNTs were dispersed in water using 1.4×10^{-2}mol/L of NaDDBS through ultrasonication for 3 hours. The fabricated cement nanocomposites presented low discreteness of electrical resistance, with relative standard deviation of less than 8%. The smaller electrical resistance discreteness indicated that the functionalized nanotubes were dispersed homogeneously within the cementitious matrix.

NOVEL ROUTES OF CNT DISPERSION

In order to avoid the problematic and time consuming process of dispersing CNTs within cementitious matrix, an innovative method of fabricating cementitious nanocomposites through growth of CNTs on to the cement particles has been recently reported by Nasibulin et al. (Nasibulin, 2009). CNTs were grown in a chemical vapour deposition (CVD) reactor at 400-700°C using acetylene as the main carbon source and carbon monoxide and dioxide as the additives to enhance the yield. Cement powder was feed in the reactor continuously at a speed of 30 g/h and the oxides (Fe_2O_3) present in the cement acted as catalysts for CNT growth, without the need for an additional catalyst support used in the conventional CVD process. The concept of preparing cement nanocomposites using this route has been illustrated in Fig. 6.

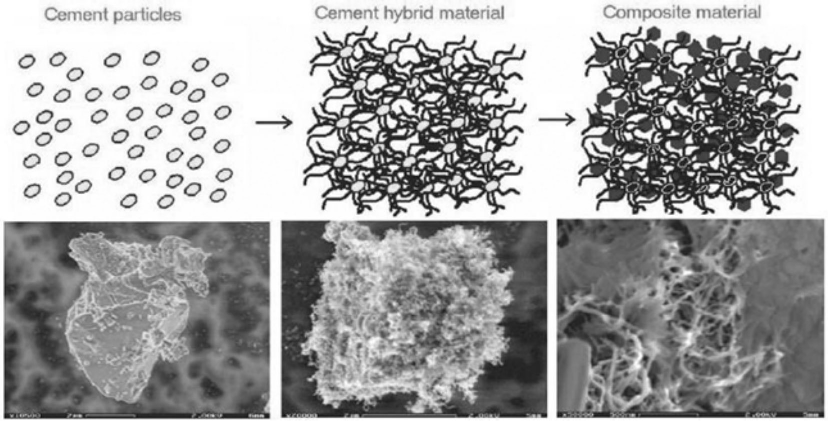

Fig. 6. Schematic diagram showing concept of incorporating CNTs/CNFs within cementitious composites by their direct growth on cement particles

The TEM images of CNT grown cement particles showed the complete coverage of cement particles by carbon nanomaterials and formation of MWCNTs as well as CNFs. In a more recent work (Mudimela, 2009), the same researchers have grown CNTs on the silica fume particles, impregnated with iron salt, using acetylene as the carbon source. CNTs with 5-10 walls and diameters of 10-15 nm were grown on silica fume particles at 600°C and with 12-20 nm diameters were produced at 750°C. Silica fume, which is used as an admixture, can therefore be utilized to introduce CNTs within cementitious matrices.

MICROSTRUCTURE OF CARBON NANOMATERIAL/CEMENT COMPOSITES

It has been reported by several researchers that carbon nanomaterials can significantly change the microstructure of cement, which is one principal reason for improvement in mechanical properties. Nochaiya et al. (Nochaiya, 2011) have studied the influence of MWCNT on the porosity and microstructure of Portland cement. MWCNTs were uniformly dispersed in water using ultrasonication for 1h, prior to mixing with cement. The porosity of Portland cement without and with CNTs, as measured using Mercury Intrusion Porosimetry (MIP), is provided in Table 1.

Table 1 MIP analysis results of PC and PC-CNT pastes after setting period of 28 days

Mixes	Total intruded volume (cm^3/gm)	Total porosity (%)	Total surface area (m^2/gm)
Portland cement (PC)	0.1717	27.1740	31.4562
PC with 0.5% CNTs	0.1494	25.5226	25.3531
PC with 1.0% CNTs	0.1422	22.7398	24.3459

It can be noticed from Table 1 that the total porosity and surface area both decreased with CNT addition. This was attributed to the fact that CNTs filled in the pores, mainly the mesopores (size less than 50 nm), between the hydration products and, thereby produced a denser microstructure than the unreinforced cement. Moreover, this also resulted in very good interaction between the hydration products and dispersed CNTs, which were seen densely inserted between the C-S-H and CH phases of cement (Fig. 7).

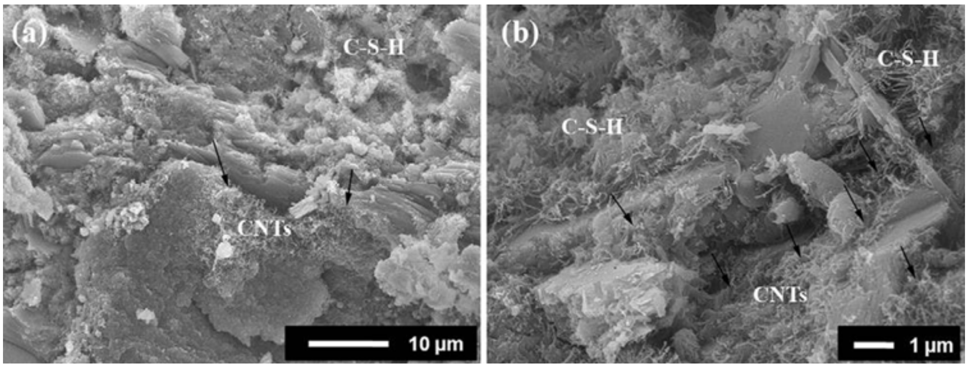

Fig. 7. SEM micrographs of 1wt.% CNT/cement paste at 28 days of hydration at different magnifications

Similar findings were also made by Li et al. from the porosity measurements of Portland cement and that containing surface treated MWCNTs (Li, 2007). Incorporation of 0.5 wt. %

CNT resulted in 64% lower porosity as compared to Portland cement. Also, the samples containing 0.5 wt. % CNT contained 82% lower pores with size more than 50 nm. On the contrary, cement composites containing carbon fibres showed much higher porosity than the Portland cement samples. Nanoindentation tests carried out by Konsta-Gdoutos et al. (Konsta-Gdoutos, 2010) also showed lower probability of porous phase in a cement nanocomposite containing 0.08 wt. % MWCNT than Portland cement, indicating lower porosity in case of nanocomposites.

MECHANICAL PROPERTIES OF CARBON NANOMATERIAL/CEMENT COMPOSITES

Early investigation by Makar et al. (Makar, 2005) showed that CNTs have strong influence on the hardness of cementitious composites. Hardness is an indirect measurement of the mechanical properties of cement based composites. Portland cement/SWCNT nanocomposites with cement/CNT ratio of 0.02 (by weight) was prepared through sonication of CNT/cement/isopropanol mixture for 4 hours, followed by removal of solvent (isopropanol) through desiccation and grounding the CNT/cement cake using a hand mortar. Although this mixing process did not ensure homogeneous dispersion of CNTs within cement matrix, the results of Vickers hardness measurement was very promising. The hardness improved up to 600% in case of 0.4 and 0.5 water/cement ratios in early hydration stages, although no improvement in hardness was observed after 14 days of hydration. This result indicated that CNT has a strong influence on the hydration process and mechanical properties of cement nanocomposites.

However, as in case of polymer, the reinforcing efficiency of carbon nanomaterials in cementitious matrices and the resulting mechanical properties of nanocomposites also depend on several critical factors. Efforts have been directed to understand and control these factors to successfully transfer the mechanical properties of nanomaterials in to composites. Konsta-Gdoutos et al. (Konsta-Gdoutos, 2010) have investigated the influence of CNT length on the macro and nano-scale mechanical properties of cement nanocomposites. According to their study, short MWCNTs (10-30 μm) provide better flexural properties when used at higher concentrations (0.08 wt. %), whereas long MWCNTs (10-100 μm) are more effective in enhancing flexural properties when used at lower concentrations (0.048 wt. %). In both the cases, good dispersion of CNTs within cement matrix was achieved using ultrasonication and a surfactant to MWCNT weight ratio of 4. The achievable improvement of flexural properties was much higher than the predicted values, and those obtained by other researchers. The reason for such high improvement in flexural properties was not only the homogeneous dispersion of MWCNTs, but also the increase in the amount of high stiffness C-S-H phases and decrease in cement porosity.

The influence of nanomaterial dispersion on the mechanical properties of cement nanocomposites has been demonstrated by several researchers. As discussed earlier, the type of surfactant has strong influence on the dispersion of CNFs/CNTs and therefore, is also very important with respect to the mechanical properties. As can be observed from Fig. 8, among the various surfactant such as sodium dodecyl benzene sulfonate (SDBS), sodium deoxycholate (NaDC), Triton X-100 (TX10), Arabic gum (AG), and cetyltrimethyl ammonium bromide (CTAB), the highest flexural and compressive properties were achieved

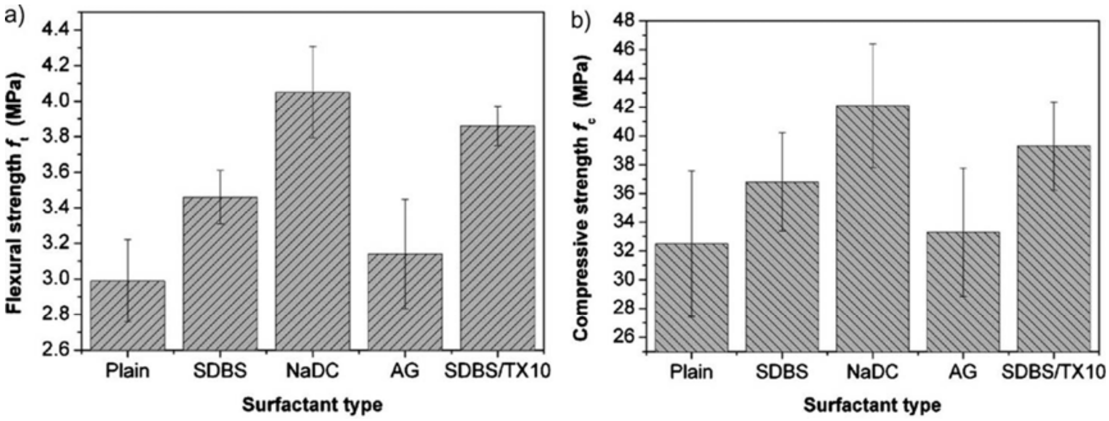

Fig. 8. Mechanical properties of plain cement and 0.2% MWCNT/cement composite prepared using various surfactants: (a) flexural strength and (b) compressive strength

with NaDC, whereas the lowest variation as well as second best flexural and compressive strengths were obtained in case of 3:1mixture of SDBS and Triton X-100 (TX10). The improvements in case of NaDC were 35.45% and 29.5% as compared to plain cement paste. The highest improvement in case of NaDC was due to good dispersion of MWCNTs as well as formation of strong interface between cement matrix and MWCNTs. Similarly, better mechanical properties in case of SDBS and Triton X-100 (TX10) mixture resulted from the best dispersion ability of this combination and also good bonding between MWCNTs and matrix. Microscopy study in case of this surfactant combination suggested that MWCNTs were well distributed within the cement matrix as a net like structure and acted as bride-transmitters between the micro-cracks, resulting in superior mechanical performance (Luo, 2009).

In a similar study by Collins et al. (Collins, 2012) it was observed that various admixtures used to improve dispersion of CNT within OPC paste can have strong influence on its workability and mechanical performance. Among the various admixtures studied, improved aqueous dispersion of CNT was observed in case of air entrainer, lignosulfonate and polycarboxylate. However, improved consistency and compressive strength was achieved only in case of polycarboxylate. In case of air entrainer and lignosulfonate, CNTs competed with the cement paste for reaction with these admixtures and thereby led to CNT agglomeration and lower consistency as well as compressive strength. On the contrary, the use of polycarboxylate resulted in homogeneous and stable CNT dispersion throughout the cement paste, due to presence of non-polar groups which dispersed the nanotubes and polar groups which dispersed water and cement. The paste containing 0.8% polycarboxylate and 0.5% CNT showed very good flow behaviour even with low water ratio (0.35) and presented a compressive strength 25% higher than the control cement samples.

Since formation of a strong interface is a prerequisite for proper load transfer between fibre and matrix and improved mechanical performance, surface functionalization of CNTs/CNFs have been tried to improve interfacial interactions between carbon nanomaterials and cementitious matrix. Formation of covalent bonding between COOH or C-OH groups of functionalized CNTs and C-S-H phases of cement matrix has been observed by Li et al. through FTIR studies (Li, 2007). This result was also supported by microscopy studies which showed tight wrapping of CNTs by C-S-H phases, indicating strong interface. The resulting cement nanocomposites containing 0.5 wt.% of surface treated MWCNT presented much better flexural and compressive properties as compared to plain cement paste, as presented in Table 2. Flexural and compressive strength improved up to 25% and 19% respectively. On the contrary, although an improvement of 22% in flexural strength was achieved with 0.5 wt.% of carbon fibres, compressive strength was deteriorated.

Table 2 Compressive and flexural strength of plain cement paste (PC) and that containing carbon fibres (CF) and surface treated MWCNT after 28 days of curing

Mix	**Compressive strength (MPa)**	**Flexural strength (MPa)**
PC	52.27 ± 1.4%	6.69 ± 1.5%
PC+ 0.5% CF	47.51 ± 3.1%	8.14 ± 2.6%
PC + 0.5% MWCNT	62.13 ± 2.3%	8.37 ± 2.1%

Use of surface treated CNTs also improves the post testing mechanical integrity of cement nanocomposites, as observed by Sanchez et al. (Sanchez, 2009). According to their study cement samples containing 0.5 wt.% surface treated CNFs maintained better structural integrity than the control samples after compression testing, as shown in Fig. 9. Similar observations were also made by the same authors in case of hybrid CNF/silica fume cement composites, where silica fume facilitated in CNF dispersion due to its small particle size. Better structural integrity in case of CNF/cement composites resulted due to the restriction in crack propagation by the entangled clumps of CNF inside cement cavities, leading to bridging of cracks and, also due to individually dispersed CNFs within the cement matrix. It was also observed that after decalcification using ammonium nitrate solution for 95 days, the samples containing CNFs showed better ductile behaviour with slow load dissipation after failure. This indicates better durability of CNF/cement nanocomposites as compared to the plain cement paste.

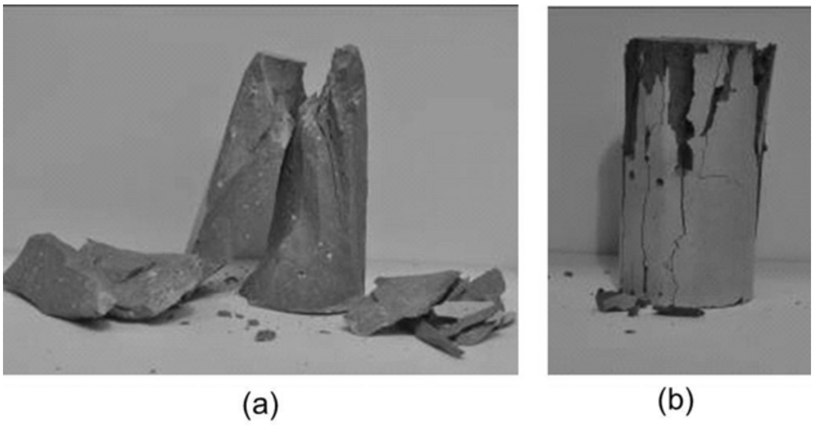

Fig. 9. Post compression testing structural integrity of plan cement paste (a) and cement paste containing 0.5 wt.% surface treated CNFs

The positive influence of surface treatment of MWCNTs on the compressive strength of cement composites was also observed by Cwirzen et al (Cwirzen, 2008). Homogenous dispersion of MWCNTs in water was obtained through wrapping by acrylic acid polymer. However, pristine MWCNTs wrapped with polymer did not show any improvement in the compressive strength of cement paste. On the contrary, cement composites containing 0.045% of MWCNT-COOHs showed nearly 50% increase in compressive strength as compared to control cement paste, due to formation of covalent bonding between functionalized CNTs and C-S-H phases of cement resulting in proper load transfer. On the other hand, gum arabic was found ineffective in improving mechanical properties of cement nanocomposites. Although, a good dispersion of MWCNTs was ensured using gum arabic, similar to acrylic acid polymer, the compressive strength was significantly lower, since gum arabic was found to be a less effective plasticizing agent for the used type of cement and also it slowed down the cement hydration process.

Functionalization of CNT through oxidation using strong acids led to formation of carboxylated carbonaceous fragments or CCFs on the surface of CNTs, as also mentioned in section 5.2.3, and their removal is necessary to improve the mechanical properties of CNT/cement nanocomposites. In the study performed by Nasibulina et al. (Nasibulina, 2012) it was observed that incorporation of functionalized CNTs (0.01 wt.%) containing CCFs resulted in only 13% improvement in compressive strength, whereas after removal of CCFs using acetone resulted in very strong improvement in compressive strength, up to 97% using only 0.03 wt.% CNT. This was attributed to the fact that functionalized CNTs became less accessible for the reaction with cement hydration products and their nucleation, due to presence of these CCFs. It was also interesting to observe in this study that the use of surfactant (4% SDS) to improve the CNT dispersion reduced the compressive strength by 65%, as the surfactant adsorbed on the CNT surface prevented the direct contact between the surface functional groups and cement hydration products.

Although surface functionalization of CNFs/CNTs was found effective for enhancing mechanical performance of cement composites by many authors, its detrimental influence has also been reported in the literature. For example, Musso et al. (Musso, 2009) prepared and compared the mechanical properties of cement nanocomposites containing 0.5 wt.% of pristine, annealed and carboxyl functionalized MWCNTs. CNTs were first dispersed in acetone through ultrasonication for 4 hours and subsequently, acetone was evaporated and CNT powder was mixed with cement, water and sand using a rotary mixer.

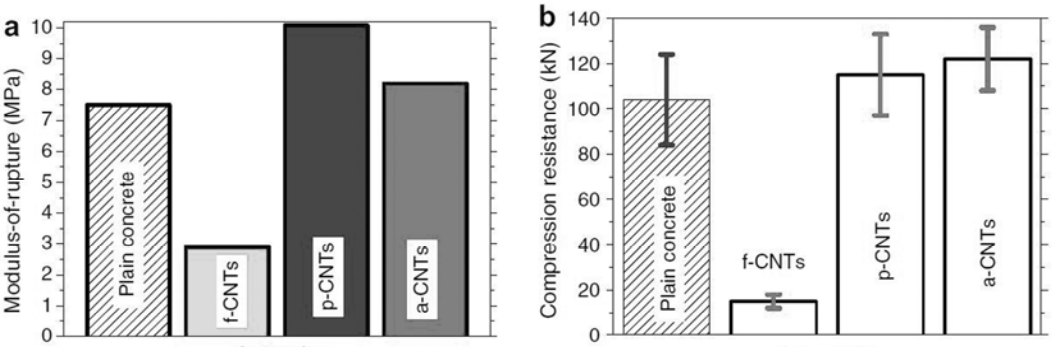

Fig 10. Modulus-of-rupture (a) and compression resistance (b) of concrete with and without MWCNTs

It was observed that the hydration of cement paste was adversely affected due to the functionalized CNTs which absorbed most of the water present in the cement paste owing to their hydrophilic nature. Thermo-gravimetric analysis showed the formation of lower amount of tobermorite gel due to improper hydration process. Mechanical properties of cement paste containing functionalized CNTs were deteriorated considerably due to this fact, whereas addition of pristine and annealed CNTs resulted in significant improvement in mechanical properties, as can be seen from Fig. 10.

MECHANICAL PROPERTIES OF NON-AUTOCLAVE FOAM CEMENT NANOCOMPOSITES

Non-autoclave foam concrete is considered as an important construction material due to its several beneficial features such as light weight, good thermal insulation and lower environmental impact. Various attempts have been made to improve the strength of foam concrete without changing its density either through increasing the amount of binding materials and decreasing the amount of mineral additives or by reinforcing the concrete matrix, In a study conducted by Yakovlev et al. (Yakovlev, 2006) it was found that the use of CNTs (0.05% by mass) as the reinforcement of foam concrete stabilized its structure by decreasing the pore wall percolation and ensuring better pore size uniformity (Fig. 11). This resulted in strong improvement in the compressive strength (70%) associated with a decrease in the average density of concrete from 330 kg/m^3 to 309 kg/m^3. This study demonstrated the possibility of producing high strength concrete without increasing its density through CNT reinforcement.

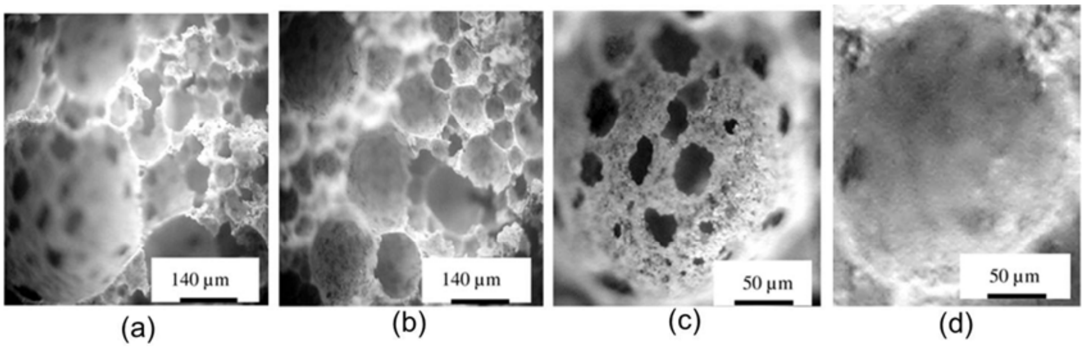

Fig. 11. Structure of cement-foam concrete: (a) without nanotubes, (b) with 0.05% CNT (pore walls), (c) without CNT (perforated) and (d) stabilized with addition of 0.05% CNT

MECHANICAL PROPERTIES OF FLY-ASH CEMENT NANOCOMPOSITES

Fly-ash cement is also considered as one of the important materials for civil constructions as it offers many advantages such as environmental benefits (by product of coal power plant), produces less heat of hydration, provide better workability and durability towards chemical attacks such as chloride and sulfates (Saraswathy, 2007). However, due to slower hydration process fly-ash cement presents lower 28 days compressive strength as compared to Portland cement. Attempts have also been made to enhance the mechanical performance of fly-ash cement using CNTs. Recently, Chaipanich et al. (Chaipanich, 2010) conducted a study by dispersing CNTs (0.5 and 1.0 wt.% of cement mixes) in a part of the mix water using ultrasonication for 10 min and then adding the suspension to the mixture of flay-ash cement, remaining water and sand to produce cement nanocomposite samples. It was observed that the fly-ash cement samples containing CNTs presented higher density than control fly-ash and PC samples. The higher density in fly-ash cement/CNT composite samples was attributed to the filling of cement pores by CNTs, resulting in a denser micro-structure. The improvement in micro-structure resulted in significant improvement of fly-ash cement composite strength with CNT addition. The compressive strength of fly-ash cement composites containing 1 wt. % CNT reached that of PC at 28 days and 60 days. However, from the TGA and DTA analysis it was confirmed that CNTs did not have any influence on the hydration process and the influence was only physical, i.e., improvement of cement micro-structure.

MECHANICAL PROPERTIES OF CEMENT/CNT HYBRID MATERIAL BASED NANOCOMPOSITES

As discussed previously, a novel type of cement nanocomposite based on CNT grown cement particles has been developed by Nasibulin et al. (Nasibulin, 2009). Mechanical properties of this cement nanocomposite were found 2 times higher than the pristine cement composites after 28 days of hydration. It was observed that the best compressive strength of CHM nanocomposites was obtained when the nanomaterials were grown in presence of $CO_{2,}$ whereas the presence of CO led to the best electrical properties. Fracture surface study by SEM showed that the CNTs and CNFs were well imbedded in to the hydration products of C-S-H phases and bridged the adjacent cement particles, resulting in strong improvements in compressive strength.

MECHANICAL PROPERTIES OF HYBRID CEMENT NANOCOMPOSITES

Development of hybrid cement nanocomposites using both carbon nanomaterials and other types of filler has also been attempted. Use of CNTs in combination with nanoclay ((nano metakaolin or NMK) has been reported by Morsy et al (Morsy, 2011). NMK is a silica based material, which can react with $Ca(OH)_2$ to produce C-S-H gel at room temperature. According to previous research findings, incorporation of NMK in to concrete can significantly improve the early strength, increase resistance to alkali-silica reaction and sulfate and can increase toughness and durability (Wild, 1996). In the study by Morsy et al. (Morsy, 2011), 6 wt.% of nanoclay was exfoliated through homogeneous mixing in ammonium chloride solution and subsequently, exfoliated nanoclay, cement and CNTs were dry mixed for 5 min to obtain a homogeneous mixture. Compressive test results after 28 days set samples showed that addition of NMK increased the compressive strength by 18% over the control mix (Fig. 12).

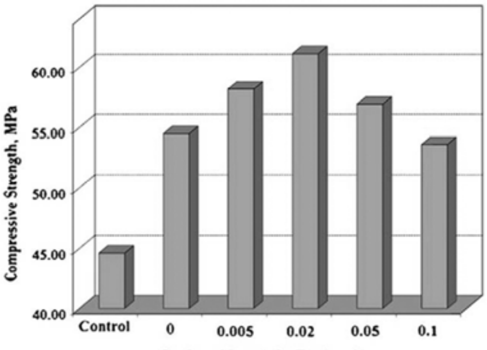

Fig. 12. Influence of CNT addition on the compressive strength of cement mortar containing 6% NMK at 28 days of hydration

The increase of compressive strength due to NMK addition was attributed to the reduced porosity and improved microstructure of cement, as the small size nano clay particles filled up the pores of cement. Moreover, NMK improved the solid volume and bond strength of cement through pozzolanic reaction between silicon and alumina elements present in NMK and the elements of calcium oxide and hydroxide in cement. Addition of CNTs to the NMK cement mortar up to 0.02% resulted in 11% higher compressive strength as compared to the mortar containing 6% NMK. SEM micrographs of samples hydrated for 28 days suggested that CNTs were individually dispersed and formed bridges between the C-S-H phases of cement, thus preventing the formation of micro-cracks. During dry mixing, the exfoliated nanoclay particles might have disrupted the attractive forces between CNTs and separated them, leading to their individual dispersion. Additionally, the presence of NMK particles mixed with the dispersed CNTs could act as a Si source for the formation of Ca-Si rich phases and, CNTs could further act as the nucleation sites for the self-assembly of Ca-Si phases. However, CNT concentration more than 0.02% resulted in agglomeration of CNTs and therefore, led to inferior microstructure and lower compressive strength.

Hybrid cement nanocomposites containing reinforcements at both micro and nano-scale have been developed by Metaxa et al (Metaxa, 2010). Polyvinyl alcohol (PVA) micro-fibres and CNFs were dispersed in to Ordinary Portland Cement and mechanical performance of hybrid nanocomposites was evaluated using fracture mechanical tests. It was observed that cement containing CNFs presented much higher load carrying capability at the same CMOD during the early stages of loading. Using only 0.048% CNFs Young´s modulus, flexural strength and toughness improved up to 75%, 40% and 35% respectively. On the contrary, use of PVA micro-fibres improved the Young´s modulus and flexural strength only marginally, but the fracture toughness increased tremendously, retaining the load for ten times higher CMOD than plain cement. Therefore, PVA micro-fibres improved the post-peak behaviour of cement resulting in a highly ductile cementitious composite. The hybrid cement nanocomposites showed higher Young´s modulus, flexural strength and toughness than plain cement, cement containing only PVA micro-fibres or CNFs. In this type, the pre-peak behaviour was mainly controlled by CNFs, whereas the post-peak behaviour was influenced by mainly PVA micro-fibres. The fracture surface study suggested good bonding between cement and both CNFs and PVA micro-fibres and bridging of micro-pores by PVA fibres and pores at nano level by CNFs. The hybrid cementitious composites showed up to 50% improvement in flexural strength, 84% improvement in Young´s modulus and 33 times (3351%) improvement in fracture toughness over plain cement matrix.

SUMMARY AND CONCLUSIONS

In this paper, current research activities on the carbon nanomaterial based cement nanocomposites have been reviewed. The major issues affecting the mechanical properties such as dispersion of nanomaterials achieved through various physical and chemical methods and microstructure of cement nanocomposites have been presented and discussed. It can be concluded from the conducted research studies that the dispersion of CNTs/CNFs within cementitious matrices is the main factor which controls the microstructure as well as the mechanical performance of the cement nanocomposites. The conventional method of mixing nanomaterials within mortar paste using a standard mixer cannot ensure homogeneous nanomaterial dispersion and therefore, deteriorates the mechanical properties. Addition of admixtures such as silica fume during the mixing process can significantly improve the nanomaterial dispersion due to mechanical separation of nanomaterials by silica fume particles. However, the best route to achieve homogeneous nanomaterial dispersion within cement composites is to disperse the nanomaterials first in water, followed by the mixing of aqueous nanomaterial dispersion with mortar paste. The various techniques attempted to achieve uniform and stable CNT/CNF aqueous dispersion are using surfactants, polymers, cement admixtures, functionalization and combination of various techniques. Surface active agents such as SDBS and its combination with Trinton-X100, polymers such as acrylic acid, cement admixtures such as polycarboxylates, nanomaterial functionalization with strong acids and combination of functionalized nanomaterials with acrylic acid polymers were found to provide very good aqueous dispersion as well as strong enhancement in mechanical properties of cementitious composites. However, unlike polymeric matrices, more care should be undertaken in case of cementitious composites to select these dispersion routes, in order to have minimum influence on the cement hydration behaviour. To avoid the dispersion problem of carbon nanomaterials within cementitious composites, a recently developed approach is based on the growth of CNFs and CNTs on cement and silica fume particles and development of cement nanocomposites using these nanomaterial grown hybrid materials. Homogeneously dispersed CNTs/CNFs leads to filling of pores within cement and improves its microstructure, restricts the propagation of nano-cracks to form micro and macro-cracks and thereby improves the fracture behaviour and mechanical properties. Multi-scale hybrid cement nanocomposites containing both mico-fibres such as PVA and CNFs are promising materials which show huge enhancements in both mechanical properties and fracture toughness. However, the research studies concerning the durability of cementitious composites containing carbon nanomaterials are very rare, and therefore, have to be carried out to a considerable extent, in order to explore the application potential of these new generation materials in construction industry.

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